Available online at www.sciencedirect.com
SCIENCE DIRECT
Science of the Total Environment 366 (2006) 851–863
Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind
www.elsevier.com/locate/scitotenv

Air–soil exchange of mercury from background soils in the United States

J.A. Ericksen, M.S. Gustin *, M. Xin, P.J. Weisberg, G.C.J. Fernandez

University of Nevada-Reno, 1664 N. Virginia St./MS 370, Reno, NV 89557, USA

Received 11 May 2005; received in revised form 10 August 2005; accepted 12 August 2005
Available online 21 September 2005

Abstract

The air–surface exchange of mercury (Hg) was measured, using a dynamic polycarbonate flux chamber, for soils with low or "background" Hg concentrations (<0.1 mg/kg) at eleven locations across the contiguous United States. Sampling locations included agricultural, desert, grassland, mixed and pine forest ecosystems ($n=1326$ soil flux measurements at 46 individual sites). An overall soil Hg flux of 0.9 ± 0.2 ng/m^2/h for these background soils was obtained by averaging the means for the different locations. Soil Hg fluxes were significantly lower in dark conditions than in the light for all but the grassland sites. Mean inlet air Hg concentrations were 1.0 ± 0.1 ng/m^3 in the dark and 1.3 ± 0.2 ng/m^3 in the light. Soil temperature inside and outside of the chamber, air temperature, relative humidity, and irradiance were measured concurrently with soil Hg flux. Soil–air Hg exchange was weakly predicted by environmental variables (R^2 from 0.07 to 0.52). For a single location, flux was better correlated with soil moisture than other measured environmental parameters, suggesting that soil moisture might be an important driver for Hg emissions from background soils. In addition, based on data collected we suggest some quality control measures for use of Tekran® 2537A analyzers when measuring low mercury fluxes. Using basic scaling procedures, we roughly estimate that natural emissions from soils in the contiguous U.S. release ~100 Mg/yr of Hg to the atmosphere.

Keywords: Mercury; Air soil exchange; Dynamic flux chambers; Quality control

1. Introduction

Previous work has shown that mercury (Hg) emissions from enriched substrates are significant sources of Hg to the atmospheric; however, little work has been done to characterize Hg air–surface exchange with low Hg containing soils. The dominant reservoir (~95%) of Hg is terrestrial systems, with the remainder stored in the oceans and atmosphere (Mason et al., 1994). The average crustal abundance of Hg is approximately 0.08 mg/kg (Mason and Moore, 1982), and the average global atmospheric concentration is approximately 1.6 ng/m^3 (Lamborg et al., 2002).

It is well established that Hg can be deposited to and emitted from terrestrial surfaces (cf. Kim et al., 1995; Poissant and Casimir, 1998; Engle et al., 2001; Zhang et al., 2001; Fitzgerald and Lamborg, 2003; Gustin, 2003; Nacht and Gustin, 2004; Mason et al., 2005). Evasion of Hg from soils appears to be driven by multiple interacting factors, such as Hg concentration and speciation in substrate, light, temperature, soil moisture, wind speed and turbulence (Kim et al., 1995; Poissant et al., 1999; Gustin, 2003; Zhang and Lindberg, 1999). Emissions from soils typically exhibit daily variability and can be

* Corresponding author. Tel.: +1 775 784 4203; fax: +1 775 784 4789.
E-mail address: msg@unr.nevada.edu (M.S. Gustin).

0048-9697/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2005.08.019

quite high in areas of natural Hg enrichment or contamination (Gustin et al., 2000). Zehner and Gustin (2002) found that the magnitude of Hg evasion from soil correlated with the substrate Hg concentration, light intensity, and temperature; they used these parameters to scale-up Hg emissions for Nevada. However, at low substrate Hg concentrations (<0.1 mg/kg) there was no log normalized relationship for Hg substrate concentration versus flux ($R^2=0.002$, $p=0.85$, $n=24$). Mercury is deposited to terrestrial surfaces from the atmosphere through both wet and dry deposition processes, and atmospherically deposited Hg may be re-emitted or recycled from a given surface back to the atmosphere (Schroeder and Munthe, 1998; Ericksen et al., submitted for publication).

Much research has focused on Hg emission from substrate with elevated Hg concentrations (Rasmussen et al., 1998; Lechler, 1999; Gustin et al., 1999; Engle et al., 2001; Gustin, 2003). Only a modest amount of Hg flux data from non-enriched, background sites have been collected (Carpi and Lindberg, 1998; Poissant and Casimir, 1998; Zhang et al., 2001; Nacht and Gustin, 2004). Because globally soils with background soil Hg concentrations constitute such a large surface area (~70–85% of terrestrial lands, Fitzgerald and Lamborg, 2003), it is imperative for developing regional and global Hg mass balances that we determine their significance as potential sources or sinks of atmospheric Hg.

This project focused on characterization of soil Hg flux at eleven non-enriched locations across the United States. A major objective of this study was to develop statistical relationships between environmental conditions and Hg flux that could be used to develop an empirical-based model for predicting and scaling Hg emissions from background soils.

2. Materials and methods

2.1. Site descriptions

Soil Hg flux over bare soil was measured at eleven background locations (Fig. 1). Table 1 lists the number of specific sampling sites at each location, the number of fluxes obtained at each site, and the Hg concentration in the soil. The locations (and specific sites) were chosen in order to obtain flux measurements from a range of different soil types. All flux measurements were made in locations that received direct sunlight except the Pine Forest and Grassland 5 sites, which were under forest and brush, respectively. For eight of the eleven sampling locations, there was one site (stationary site) where fluxes were monitored for a longer period of time, and several (satellite) sites where 1 to 4 h flux measurements were made (see Table 1).

The Agricultural site located near Underwood, North Dakota had mollisol soils (fine-loamy, typic argiborolls) with a distinct organic matter layer. Desert 1 sites were located in the arid Mohave Desert of southern California with sparse vegetation and aridisol soils (loamy, lithic camborthids). The Desert 2 sites were located in Hungry Valley in northwestern Nevada with aridisol soils hosting sparse vegetation, including few grasses and perennial forbs.

The grassland sampling locations consisted of flat or gentle rolling terrain with approximately 20% bare soil. The Grassland 1 sites were located in a mixed

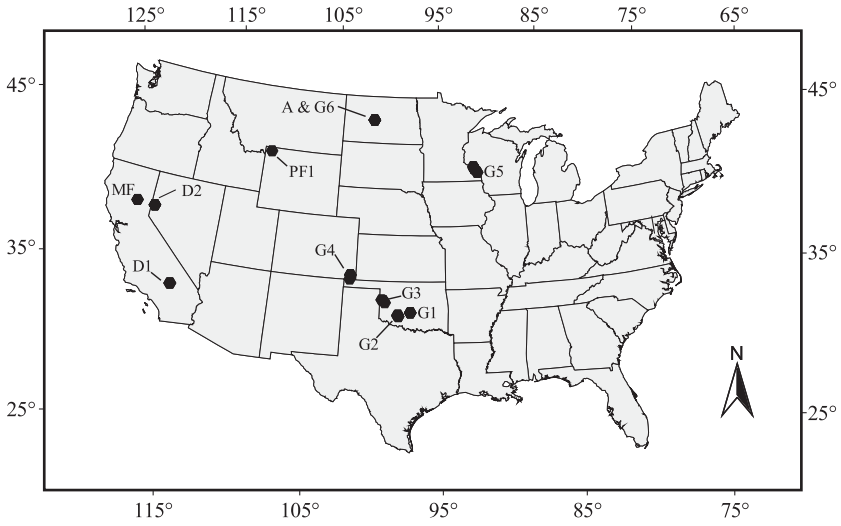

Fig. 1. Map of site locations. See Table 1 for Site Abbreviations.

Table 1
Latitude (LAT) and longitude (LON) coordinates for the sampling locations of the different sites with number of soil Hg flux measurements (#obs) and soil Hg concentrations (Soil Hg) given

SITE	Sampling location	#obs	LAT	LON	Soil Hg (mg/kg)
Agricultural	A-1	3	47° 26′ 36.5″	−101° 11′ 7.4″	0.035
	A-2	3	47° 26′ 36.6″	−101° 11′ 7.6″	0.031
	A-3	3	47° 26′ 36.6″	−101° 11′ 7.6″	0.031
	A-4	3	47° 26′ 36.6″	−101° 11′ 10.9″	0.029
Desert 1	D1-1	47	35° 3′ 53.3″	−117° 0′ 54.4″	0.032
	D1-2	7	35° 3′ 25.9″	−117° 1′ 51.2″	0.012
	D1-3	6	35° 3′ 46.4″	−116° 58′ 2.7″	0.012
	D1-4	6	35° 3′ 39.3″	−116° 59′ 36.0″	0.026
Desert 2	D2-1	547	39° 45′ 57.7″	−119° 43′ 47.7″	0.030
	D2-2	68	39° 46′ 4.3″	−119° 43′ 50.8″	0.030
	D2-3	4	39° 46′ 4.0″	−119° 43′ 53.1″	0.030
	D2-4	4	39° 46′ 4.0″	−119° 43′ 54.0″	0.030
	D2-5	4	39° 46′ 4.1″	−119° 43′ 52.6″	0.030
Grassland 1	G1-1	12	34° 58′ 58.8″	−97° 31′ 31.2″	<0.010
	G1-2	12	34° 59′ 6.1″	−97° 31′ 26.6″	0.022
	G1-3	12	34° 58′ 51.1″	−97° 31′ 19.8″	0.012
	G1-4	80	34° 59′ 4.0″	−97° 31′ 20.9″	0.017
Grassland 2	G2-1	12	34° 49′ 55.5″	−98° 31′ 38.8″	0.017
	G2-2	12	34° 46′ 57.5″	−98° 33′ 59.8″	0.016
	G2-3	64	34° 43′ 17.9″	−98° 29′ 13.5″	0.020
	G2-4	6	34° 43′ 27.5″	−98° 28′ 34.2″	0.011
Grassland 3	G3-1	10	35° 36′ 4.9″	−99° 36′ 11.7″	0.010
	G3-2	12	35° 44′ 30.7″	−99° 46′ 9.5″	<0.010
	G3-3	77	35° 46′ 16.5″	−99° 50′ 22.5″	<0.010
	G3-4	12	35° 44′ 9.8″	−99° 42′ 51.4″	<0.010
Grassland 4	G4-1	10	37° 0′ 30.5″	−102° 34′ 24.9″	<0.010
	G4-2	12	37° 0′ 30.5″	−102° 31′ 30.1″	<0.010
	G4-3	12	37° 14′ 19.8″	−102° 31′ 30.4″	0.019
	G4-4	21	37° 17′ 11.7″	−102° 31′ 32.1″	0.017
Grassland 5	G5-1	5	44° 17′ 6.0″	−91° 53′ 38.4″	0.028
	G5-2	6	44° 16′ 41.5″	−91° 52′ 56.6″	0.014
	G5-3	57	44° 21′ 29.8″	−91° 56′ 16.9″	<0.010
	G5-4	6	44° 26′ 19.6″	−91° 58′ 45.1″	<0.010
	G5-5	6	44° 1′ 21.8″	−91° 38′ 30.4″	0.013
	G5-6	6	44° 17′ 26.7″	−91° 52′ 19.8″	0.020
	G5-7	17	44° 18′ 4.0″	−91° 54′ 26.3″	0.013
	G5-8	6	44° 3′ 28.3″	−91° 38′ 4.0″	<0.010
	G5-9	6	44° 19′ 19.2″	−91° 54′ 26.1″	<0.010
Grassland 6	G6-1	4	47° 26′ 37.2″	−101° 11′ 49.4″	0.055
	G6-2	3	47° 26′ 37.2″	−101° 11′ 49.5″	0.049
	G6-3	4	47° 26′ 37.3″	−101° 11′ 49.5″	0.042
Mixed forest	MF-1	42	39° 49′ 8.5″	−121° 16′ 42.7″	0.036
	MF-2	7	39° 48′ 58.2″	−121° 16′ 37.4″	0.032
	MF-3	7	39° 21′ 1.4″	−121° 38′ 36.6″	0.048
	MF-4	6	39° 20′57.2″	−121° 38′ 45.5″	0.060
Pine forest	PF-1	57	47° 26′ 36.5″	−110° 29′ 23.7″	0.040

prairie in central Oklahoma with mollisol soils (fine-loamy, udic argiustolls), and the Grassland 2 sites were located near the Wichita Mountains in Oklahoma with mollisol soils (clayey-skeletal, udic argiustolls). The Grassland 3 sites were in the Black Kettle Grasslands Preserve near Cheyenne, Oklahoma with inceptisol soils and some alfisol soils (mixed, loamy, ustochrepts and paleudalfs) and two basic land cover types: grassland and shinnery-oak. The Grassland 4 sites were located on a flat prairie in the Cherokee National Grasslands in southeastern Colorado with mollisol and aridisol soils (mixed fine and coarse loamy, ustollic haplargids and aridic argiustolls). The Grassland 5 location was located in Wisconsin with mollisol and alfisol soils (fine-silty and fine-loamy, cumulic and typic haplaquolls), and the Grassland 6 location in North Dakota had a rich organic horizon with mollisol soils (fine-loamy, typic argiborolls).

The Mixed Forest sites were in the foothills of the northern Sierra Nevada Mountains in California and had ultisol soils (clayey, xeric haplohumults) with an organic horizon consisting of humus and pine litter. The soil Hg flux was measured adjacent to mixed hardwood and pine forest in a clearing so that no trees obstructed or shaded the site during the measurements. The Pine Forest site was located in Yellowstone National Park on the north end of the town Canyon within a stand of lodge-pole pine (moderately closed canopy), and had entisol soils (sandy-skeletal, alfic cryorthents) with a thick organic horizon underlain by a Quaternary rhyolite flow.

2.2. Field measurements

Mercury fluxes were measured using a dynamic flux chamber (DFC), which consisted of a cylindrical polycarbonate vessel with a radius of 10 cm, a height of 3.5 cm, a 1-L volume, and 16 holes (1 cm diameter) around the circumference to allow unrestricted airflow (Engle et al., 2001). The inlet line was positioned just above an inlet air port (~2 cm above the soil surface) and the outlet line was connected to the center of the top of the chamber. Only for the Pine Forest site was a 2.4-L rectangular ($20.4 \times 20.1 \times 6.5$ cm, $w \times l \times h$) polycarbonate used. This chamber had six 1.5 cm holes on one side of the chamber (the inlet) and air was pulled through two holes on the opposite side of the chamber (the outlet) (Engle et al., submitted for publication). The chamber was aligned in the field so that the inlet side was perpendicular to the dominant wind direction. At each site the DFC was placed on a bare soil surface with as little soil disturbance as possible. The outlet and inlet air streams were sampled in duplicate and averaged using a Tekran® (Model 2537A) with automated dual sampling unit. Atmospheric Hg was collected over 5 min intervals. Twenty minute Hg flux values were determined using the following equation:

$$F = Q^*(C_o - C_i)/A, \quad (1)$$

where F is the total Hg flux of the soil in ng/m^2/h, C_o and C_i are the Hg concentration of the outlet and inlet air streams in ng/m^3, A is the surface area enclosed by the DFC in m^2, and Q is the flow of ambient air through the flux chamber in m^3/h. Positive flux values indicate Hg emission from the soil into the air; whereas, negative flux values represent Hg deposition to the soil from the air. Flow was 1.5 L/min for the cylindrical DFC (turnover time 0.7 min) and 1.0 L/min for the rectangular chamber (turnover time 2.4 min). Inlet air was sampled at the same flow (Q) as the outlet stream, and the inlet concentration was calculated by averaging the inlet measured before and after two outlet measurements. When sampling, the initial flux measurements were often higher than subsequent measurements, presumably due to the effect of soil disturbance when positioning the chamber. Because this was fairly consistently observed, these flux measurements were removed from the data set.

Materials used for measurement of Hg flux underwent a rigorous cleaning procedure which included rinsing with a chelating detergent (Microsoap 90, International Products), and soaking in nitric acid solution (5–10% v/v). Before collecting soil flux measurements, chamber blanks were routinely determined by placing the DFC on a flat polycarbonate surface and measuring flux. Chamber blanks averaged 0.1 ± 0.1 ng/m^2/h and were not subtracted when calculating soil flux values. The detection limit for the Tekran mercury analyzer was 0.1 ng/m^3.

Concurrent 5-min measurements of soil temperature inside and outside the chamber (Omega Thermocouples), air temperature and relative humidity (Vaisala CS105), and incident light (LiCOR LI200X) were collected and averaged using a data logger (Campbell Scientific CR10X and CR23X).

After the flux was measured at each site, a sample of the top 2 cm of substrate was collected and stored in Ziplock™ bags. Following aqua regia digestion, the soil was analyzed for total Hg by the Nevada Bureau of Mines and Geology using cold vapor atomic absorption spectroscopy (Lechler, 1999). For one of the sites (Desert 2), the gravimetric percent water was also determined.

Statistical analysis was performed using SAS®9.1 statistical software. Simple linear and robust multiple linear regressions (MLR) were performed in an attempt

to predict Hg exchange with background soils as a function of air Hg concentration, air and soil temperatures, relative humidity, and solar irradiance. Because temperatures (soil temperature in chamber, soil temperature outside chamber, and air temperature) were strongly correlated ($r > 0.75$), only the air temperature was used in the MLR analysis. When MLR was performed on data collected in dark conditions, the light variable was not considered. Based on chi-square values from the robust MLR, we ranked parameters according to their importance or contribution in the MLR model. ANOVA and t-tests were performed in StatView™ version 5.0.1 (SAS Institute Inc.). Error bars and ± symbols in text indicate one standard error, and results were considered statistically significantly significant when $p < 0.05$.

Consecutive sampling of Grasslands 1 through 4 sites was performed during the course of one trip (07/24/03 to 08/3/03). After scrutinizing the data, we became concerned because the inlet air Hg concentrations (see Fig. 4) and soil Hg flux values decreased as sampling progressed from site 1 to 4. One factor that could have affected the air Hg concentrations would be passivation of the gold cartridges in the Tekran® 2537A analyzer. When passivation occurs, presumably due to volatile organic compounds or other atmospheric oxidants (i.e., Cl^-, NO_3^-) coating the gold traps, instrument internal calibration may appear normal (peak areas seem reasonable), and manual injections of Hg in a zero-air stream into the analyzer can have full or nearly full recovery. However, when manual injections of Hg are performed using ambient air, recovery can be very low (40–80%). This is typically resolved by cleaning the traps with methanol, dilute nitric acid, and ultrapure water. Placing a verifiably clean soda lime trap in the sample air stream just before the Tekran may

Table 2
Mean, standard error, minimum, and maximum soil Hg flux values (ng/m^2/h) and inlet air Hg concentrations (ng/m^3) for all sites combined (ALL) as well as for individual sites

Site	Descrip	#Obs	Mean flux	St err flux	Min flux	Max flux	Mean inlet	St err inlet	Min inlet	Max inlet
ALL	both	1326	**0.7**	0.03	−1.5	9.7	**1.1**	0.01	0.2	4.0
Desert 1	both	66	**0.6**	0.07	0.0	2.7	**1.4**	0.02	0.7	2.0
Desert 2	both	627	**0.2**	0.03	−1.5	4.2	**1.3**	0.01	0.2	4.0
Grassland 1	both	116	**2.5**	0.14	0.3	9.7	**1.1**	0.01	0.5	3.2
Grassland 2	both	95	**1.4**	0.09	−0.1	3.4	**0.8**	0.01	0.6	1.3
Grassland 3	both	110	**1.0**	0.06	0.1	3.5	**0.8**	0.01	0.5	1.5
Grassland 5	both	115	**0.3**	0.07	−0.9	3.5	**1.3**	0.02	0.7	3.2
Mixed forest	both	102	**1.1**	0.10	−0.2	3.8	**1.4**	0.02	1.0	2.3
Pine forest	both	57	**0.3**	0.10	−0.3	3.7	**1.0**	0.01	0.7	1.4
ALL	dark	462	**0.3**	0.04	−1.5	4.7	**1.1**	0.01	0.2	2.4
Desert 1	dark	28	**0.2**	0.02	0.0	0.5	**1.3**	0.03	1.1	1.5
Desert 2	dark	250	**0.0**	0.03	−1.5	1.3	**1.1**	0.03	0.24	2.4
Grassland 1	dark	30	**2.7**	0.18	0.3	4.7	**1.2**	0.03	0.8	2.1
Grassland 2	dark	31	**1.2**	0.05	0.6	1.8	**0.6**	0.01	0.5	0.8
Grassland 3	dark	29	**0.7**	0.07	0.1	1.5	**0.5**	0.02	0.4	0.7
Grassland 5	dark	38	**0.0**	0.03	−0.3	0.4	**1.3**	0.02	1.1	1.5
Mixed forest	dark	25	**0.5**	0.03	0.0	0.8	**1.1**	0.01	1.1	1.3
Pine forest	dark	31	**−0.1**	0.02	−0.3	0.1	**0.9**	0.06	0.7	1.1
ALL	light	848	**0.8**	0.04	−1.4	9.7	**1.2**	0.01	0.2	4.0
Agricultural	light	12	**1.2**	0.52	−1.4	5.0	**2.3**	0.08	1.4	3.7
Desert 1	light	38	**0.9**	0.10	0.0	2.7	**1.4**	0.03	0.7	2.0
Desert 2	light	377	**0.4**	0.05	−1.0	4.2	**1.4**	0.02	0.3	4.0
Grassland 1	light	86	**2.4**	0.17	0.5	9.7	**0.8**	0.01	0.5	2.0
Grassland 2	light	64	**1.5**	0.13	−0.1	3.4	**0.7**	0.01	0.5	1.0
Grassland 3	light	81	**1.1**	0.08	0.1	3.5	**0.6**	0.01	0.4	1.1
Grassland 4	light	39	**0.5**	0.05	0.2	1.1	**0.4**	0.01	0.3	0.5
Grassland 5	light	77	**0.5**	0.09	−0.9	3.5	**1.3**	0.03	0.7	3.2
Grassland 6	light	11	**0.1**	0.09	−0.2	0.8	**1.8**	0.05	1.5	2.0
Mixed forest	light	37	**1.5**	0.18	−0.3	3.8	**1.5**	0.03	1.0	2.3
Pine forest	light	26	**0.7**	0.18	−0.1	3.7	**1.6**	0.01	1.4	0.9

Summary data is given for data collected in both dark and light conditions (both), only dark conditions (dark), and only light conditions (light).

also help. Inlet air Hg concentrations are often a good indicator of trap passivation. Upon closer examination of the Tekran data, we discovered that at Grassland sites 1 through 4, one of the two gold cartridges used to sequentially collect Hg reported much lower (40% to 80% less) values than the other and was presumably passivated; and for this reason, only one trap's data was used to calculate flux. The range and mean of fluxes measured at Grasslands 1, 2, and 3 sites are not unusually low and are similar to the other sites, leading us to feel confidant in these data. However, data from the Grassland 4 site are abnormally low (e.g., air Hg concentrations were 0.40 ± 0.07) and may under represent actual air Hg concentrations and soil Hg fluxes from those areas. For that reason we have decided to err on the side of caution and exclude the Grassland 4 site when estimating an overall background soil Hg flux value.

3. Results

In this study 1326 flux measurements were collected at eleven different locations with a total of 46 different sampling sites in the United States. A 24-h or partial diel measurement of soil Hg flux was collected at each area except, the Agricultural, Grassland 4, and Grassland 6 sites where data were collected in light conditions only for 4, 18, and 4 h, respectively. Table 2 lists summary statistics for soil Hg flux (ng/m^2/h) and air Hg concentration (ng/m^3) at the different sites, as well as separate summary statistics for measurements made in dark and light conditions. The Desert 2 location had the largest and most comprehensive data set with 627 flux measurements (including six 24-h measurements) obtained for the most part monthly over the course of a year (05/03 to 05/04). The Agricultural and Grassland 6 sites were located in North Dakota had the highest air Hg concentrations of all the sites. Fig. 2 shows data from 24-h flux measurements at various sites.

Fluxes were averaged when irradiance was greater than 600 W/m^2 (to approximate midday flux) and compared with substrate concentration. A base 10 log was applied to the averaged flux and substrate Hg concentration values. Substrate values less than detection and negative flux values ($n=3$) were excluded. Regression between the variables provided the following equation ($R^2=0.26$, $p=0.01$):

$$\log \text{ soil Hg flux}\left(\text{ng/m}^2\text{/h}\right) = -1.0[\log \text{ soil Hg conc.(mg/kg)}] - 1.7. \quad (2)$$

For the most part, significant differences in soil Hg flux between the various sites were observed (Table 3). In general, soil Hg flux was significantly lower in dark conditions (<1 W/m^2) than in light (>1 W/m^2) conditions, with the exception of the Grassland 1 and 2 sites (Tables 2 and 3). Data collected right at the transition from dark to light were excluded from the comparison. Because mean Hg fluxes differed significantly for the different grassland sites as well as for the desert sites, sites with similar ecosystem types were kept separate for correlation and regression analysis.

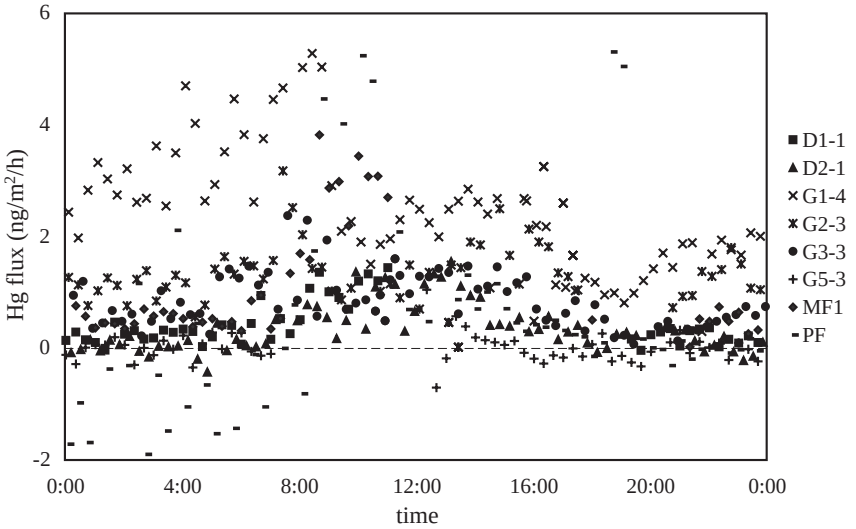

Fig. 2. Plot of soil Hg flux at the Desert 1-1 (D1-1), Desert 2-1 (D2-1), Grassland 1-4 (G1-4), Grassland 2-3 (G2-3), Grassland 3-3 (G3-3), Grassland 5-3 (G5-3), Mixed Forest 1 (MF1), and the Pine Forest (PF) sites as a function of time.

Table 3
Statistical data for multiple linear regression analysis (MLR, R^2 values) performed using inlet (I) air Hg concentration, air temperature (T), relative humidity (r), and light (L) parameters

Site	Descrip	MLR R^2	Order of import.	%Out	#Obs	Not sign. different
Desert 1	both	0.25	L I R A	9.1	66	
Desert2	both	0.12	R I T L	11	627	a
Grassland 1	both	0.31	I T R L	6.9	116	
Grassland 2	both	0.22	I L T R	16	95	
Grassland 3	both	0.07	L I T R	9.9	110	b
Grassland 5	both	0.17	L T R I	14	115	c
Mixed forest	both	0.12	R I T L	13	102	b
Pine forest	both	0.41	L I T R	9	57	a, c
Desert 1	dark	0.33	T I R	18	28	
Desert 2	dark	0.17	R I T	3.6	250	d
Grassland 1	dark	0.44	I R T	13	30	**k**
Grassland 2	dark	0.22	T R I	3.3	31	**m**
Grassland 3	dark	0.15	T R I	6.7	29	
Grassland 5	dark	0.33	I T R	21	38	d
Mixed forest	dark	0.31	I T R	20	25	
Pine forest	dark	0.26	I T R	3.2	31	d
Agricultural	light	0.52	L I T R	42	12	e, f, g, h
Desert 1	light	0.21	I L T R	18	38	e, h
Desert 2	light	0.19	R T L I	9.3	377	i
Grassland 1	light	0.33	I R L T	4.7	86	**k**
Grassland 2	light	0.32	L R T I	20	64	f, **m**
Grassland 3	light	0.08	L I T R	12	81	e
Grassland 4	light	0.12	I L R T	0.0	39	i
Grassland 5	light	0.21	I L T R	7.8	77	i, j
Grassland 6	light	0.42	R T L I	36	11	g, j
Mixed forest	light	0.34	R T I L	16	37	f
Pine forest	light	0.42	L I R T	19	26	g, h, i, j

The parameters are listed in order of importance to the MLR model based on chi-square values. The percent of observations (#Obs) that were considered outliers (%Out) based on normality and skewness tests are reported. Fluxes from sites with both light and dark data, only dark, and only light were compared, as well as dark and light data from the same site. Data sets that did not have significantly different ($p > 0.05$) Hg fluxes are designated by similar letters in the right most column. The bold letters highlight that dark and light fluxes for Grassland sites 1 and 2 were not significantly different.

Statistical analysis comparing fluxes from stationary sites with satellite sites in similar light conditions indicated that soil Hg fluxes were not significantly different for five of the eight sites. Flux values from stationary and satellite sites at the Desert 1, Grassland 2, and Mixed Forest locations were significantly different.

Fig. 3 illustrates the relative frequency distribution of the soil Hg flux measurements in dark and light conditions at the various sites. The bulk (83%) of the soil Hg flux measurements were between 0 and 2 ng/m^2/h and in general, the dominant flux was emission. Atmospheric deposition of Hg (negative flux values) was observed at the Desert 2, Grassland 5, and Pine Forest sites. The lowest minimum soil Hg flux measured was -1.5 ng/m^2/h at the Desert 2 location in dark conditions, and the greatest maximum flux measured was 9.7 ng/m^2/h at the Grassland 1 site in light conditions. Fig. 4 further illustrates the mean inlet air Hg concentrations measured at each location.

Multiple linear regression (MLR) models were constructed for soil Hg flux using the air Hg concentration, air temperature, relative humidity, and light as variables, and R^2 values for the full model (representing variance explained by all variables) are reported in Table 3. Data sets were checked for normality and skewness, and the percent of highly influential outliers are reported; however, outliers were included in all statistical analysis since there was no justifiable reason to exclude them. All R^2 values for the MLR analysis are less than 0.5, with the exception of the Agricultural site ($R^2 = 0.52$). Table 3 describes significant differences between sites where fluxes were measured in both dark and light conditions, as well as differences between dark and light flux data measured from the same site.

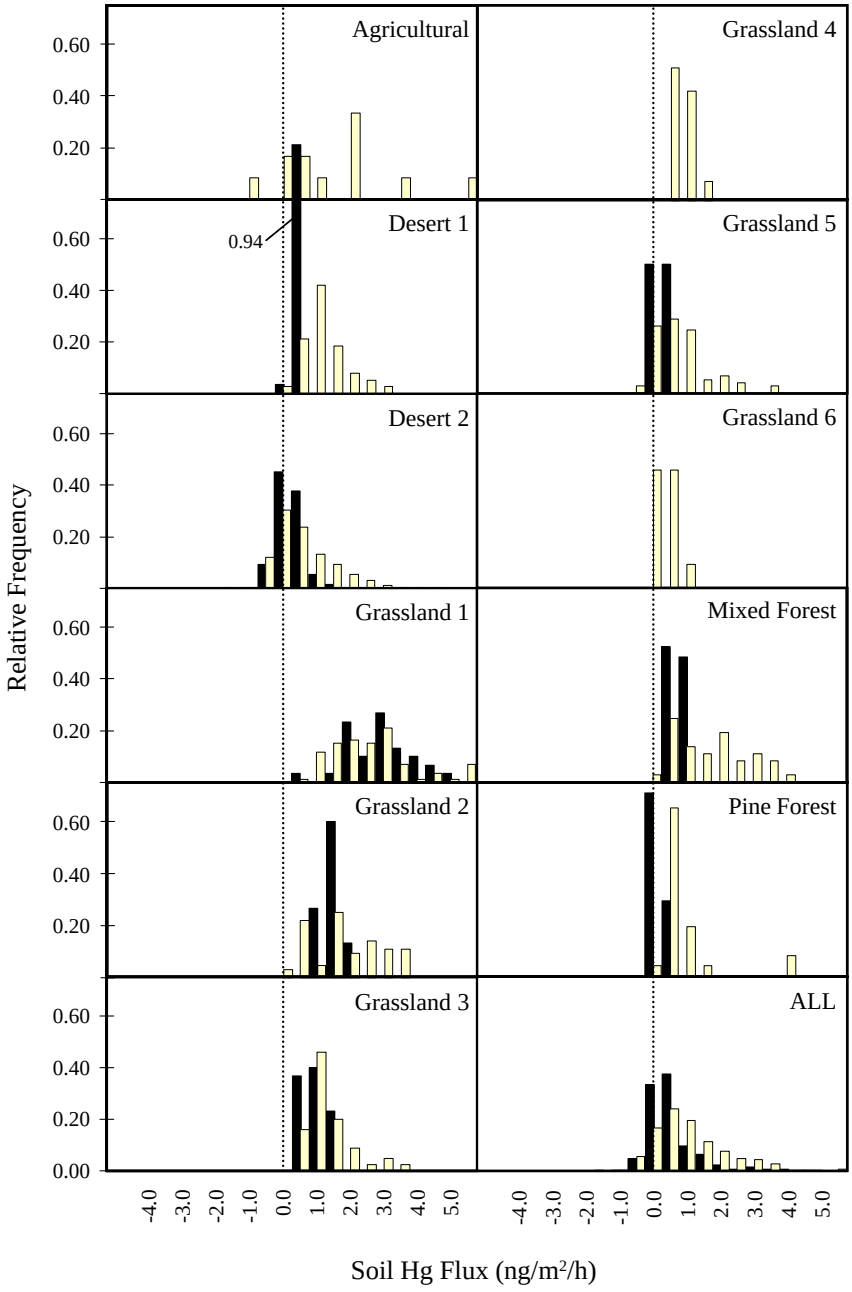

Fig. 3. Histograms of relative frequency of soil Hg flux in dark (dark bars) and light (light bars) conditions at each site and all sites.

Simple linear correlations were performed between soil Hg flux and all measured parameters (inlet air Hg concentration, soil temperature inside and outside the chamber, air temperature, relative humidity, and irradiance) for dark and light data, separately and combined for each individual site and all sites combined. These correlation coefficients are listed in Table 4. All 166 *r*-values are between −0.7 and 0.7 except for five values, four of which are correlation coefficients observed at the Grassland 1 site in dark conditions, and one from the Agricultural site in light conditions.

Additionally, the mean midday soil Hg flux (measured between 11:00 and 13:00) at the Desert 2 site as a function of percent soil moisture (by weight) is plotted in Fig. 5. Here we observed a positive correlation (R^2=0.66) between percent soil moisture and soil Hg flux. The mean irradiance was between 600 and 1100 W/m^2 for all measurements with the excep-

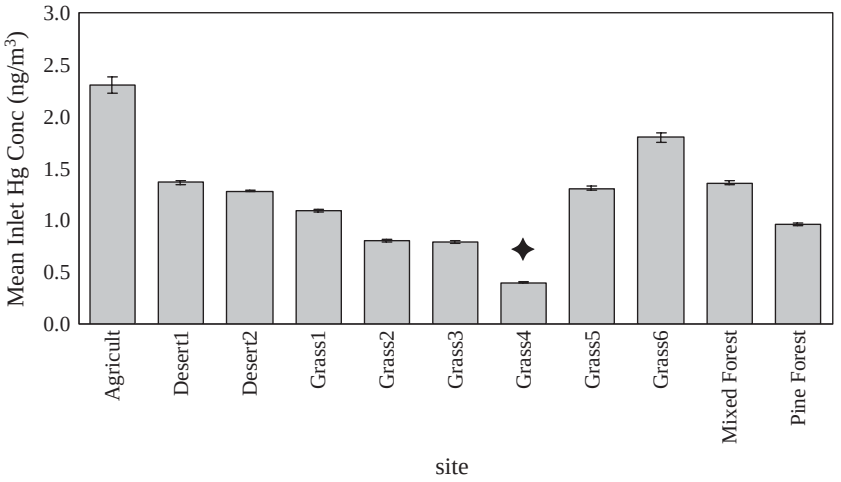

Fig. 4. Bar graph of mean inlet air Hg concentrations at each site. Bar with ✦ highlights the sampling location where there may be have been instrumentation problems (see text for discussion). Error bars represent ± one standard error.

tion of a measurement made in December 2003 with 13% soil moisture and an irradiance of 400 W/m^2. The correlation between soil Hg flux and soil moisture increases if the December measurement with low solar irradiance is removed (R^2=0.78) or if the soil Hg flux is normalized by the light intensity (R^2=0.82).

4. Discussion

Excluding data from Grassland 4 (see Materials and Methods section), the average of the mean air Hg concentration for the sites was 1.0 ± 0.3 ng/m^3 in dark conditions, 1.3 ± 0.5 ng/m^3 in light conditions, and 1.3 ± 0.5 ng/m^3 overall (both dark and light conditions). Similarly, the average of mean soil Hg flux was 0.6 ± 0.9 ng/m^2/h in dark, 1.0 ± 0.7 ng/m^2/h in light, and 0.9 ± 0.7 ng/m^2/h overall. Mean soil Hg fluxes for each site in this study ranged from −0.1 to 2.7 ng/m^2/h and are comparable in magnitude to those reported by other studies conducted in background locations, which ranged from −0.02 to 13 ng/m^2/h (Schroeder et al., 1989; Xiao et al., 1991; Kim et al., 1995; Lindberg et al., 1998; Poissant and Casimir, 1998; Carpi and Lindberg, 1998; Zhang et al., 2001; Nacht and Gustin, 2004).

For the most part, there were significant differences in soil Hg flux between the different sampling locations (Table 3), and there were no consistent trends of soil Hg flux as a function of ecosystem type. For example, the desert sites had dissimilar fluxes even though the two respective environments had similar air and soil Hg concentrations. Desert 1 was located in the Mohave Desert (a very arid desert) and was sampled in July, and Desert 2 was located in Nevada (a semi-arid desert) and was sampled monthly. When only the July data for Desert 2 site is compared with the Desert 1 data, the sites still have significantly different soil Hg fluxes. Grassland 1 through 4 sites showed a steady decrease in air Hg concentrations and fluxes, which may have been attributed to trap passivation. Grassland sites 1 through 4 were sampled at the beginning of August, and Grassland 5 and 6 were sampled in September and October, respectively. Maximum solar irradiance and mean soil temperature were ~75% less for Grassland 5 and 6 than Grasslands 1 through 4; however, this cannot account for the flux differences. Grassland 6 had the highest air Hg concentrations and the lowest soil Hg flux of the six grasslands sampled. At this time we do not have a definitive answer to account for differences of soil Hg flux from similar ecosystem types but hypothesize that soil properties and atmospheric chemistry (Engle et al., in press) may be responsible.

The Desert 1 and Mixed Forest sites had different soil types (aridisol and ultisol, respectively) but both were underlain by Mesozoic granitic rock lithology. The Desert 1 site had a mean soil Hg flux of 0.6 ± 0.6 ng/m^2/h; whereas the Mixed Forest site had a higher mean soil Hg flux of 1.1 ± 1.0 ng/m^2/h. The sampling programs for these two specific sites were designed so that simple ANOVA analysis could be used, and the two sites were found to be significantly different (p<0.001), suggesting that soil type may be important in controlling soil Hg flux.

Regression models using soil Hg concentration vs. flux and the MLR analysis only weakly predicted soil Hg flux. The log regression between average midday

Table 4
Simple linear correlation coefficient (r) values between Hg flux and inlet air Hg concentrations (Inlet), flux chamber temperature (FC T), soil temperature (Soil T), air temperature (Air T), relative humidity (RH), and light (Light)

Site	Descrip	Pearson correlation coefficient (r)					
		Inlet	FC T	Soil T	Air T	RH	Light
Desert 1	both	0.53 s	0.59 s	0.28 s	0.23 s	−0.31 s	0.67 s
Desert 2	both	0.45 s	−0.08	0.25 s	−0.10 s	0.30 s	0.16 s
Grassland 1	both	0.45 s	−0.23	−0.08	−0.10	0.13	−0.04
Grassland 2	both	0.19	0.40 s	0.14 s	0.20	−0.20	0.46
Grassland 3	both	0.14	0.10	0.06	0.06	0.06	0.17
Grassland 5	both	0.25 s	0.39 s	0.53 s	0.23 s	−0.28 s	0.62 s
Mixed forest	both	0.34 s	–	–	0.39 s	−0.57 s	0.52 s
Pine forest	both	0.38 s	0.44 s	0.44 s	0.51 s	−0.43 s	0.33 s
Desert 1	dark	−0.20	−0.06	−0.06	−0.05	−0.03	
Desert 2	dark	0.46	−0.37 s	−0.35 s	0.37 s	0.50 s	
Grassland 1	dark	0.55 s	−0.80 s	−0.80 s	−0.78 s	0.79 s	
Grassland 2	dark	0.13	−0.19	−0.21	−0.17	0.03	
Grassland 3	dark	0.50 s	−0.53 s	−0.56 s	−0.54 s	0.52 s	
Grassland 5	dark	−0.19	−0.20	−0.19	−0.19	0.16	
Mixed forest	dark	−0.56 s	–	–	−0.21	0.11	
Pine forest	dark	−0.55 s	0.37 s	0.38 s	0.37 s	−0.39 s	
Agricultural	light	−0.34	0.24	0.15	0.44	−0.40	−0.71s
Desert 1	light	0.47 s	0.30	0.00	−0.11	0.05	0.42 s
Desert 2	light	0.43 s	−0.25 s	−0.36 s	−0.22 s	0.50 s	0.00
Grassland 1	light	0.48	−0.06	0.25	−0.02	0.02	0.00
Grassland 2	light	0.15	0.56 s	0.15	0.12	−0.13	0.53 s
Grassland 3	light	0.03	−0.12	−0.03	−0.17	0.21	−0.02
Grassland 4	light	0.55	−0.06	−0.38 s	−0.29	0.28	−0.40 s
Grassland 5	light	0.27 s	0.24 s	0.49 s	−0.03	−0.04	0.56 s
Grassland 6	light	0.49	0.12	0.32	0.56	−0.54	0.50
Mixed forest	light	0.07	–	–	0.08	−0.39 s	0.25
Pine forest	light	0.06	−0.08	−0.08	0.32	−0.01	0.01

Soil temperature data was not available for the Mixed forest site, and correlations between measured light and Hg soil flux were not performed in dark conditions. All r-values with the letter s were statistically significant ($p<0.05$).

flux and substrate Hg concentration had a R^2 value of 0.26 (Eq. (2)). The R^2 values for MLR models ranged from 0.07 to 0.52 with the Agriculture, Grassland 6, and Pine Forest sites having the highest R^2 values (Table 3). The Agriculture and Grassland 6 sites had the least amount of soil Hg flux measurements ($n=12$

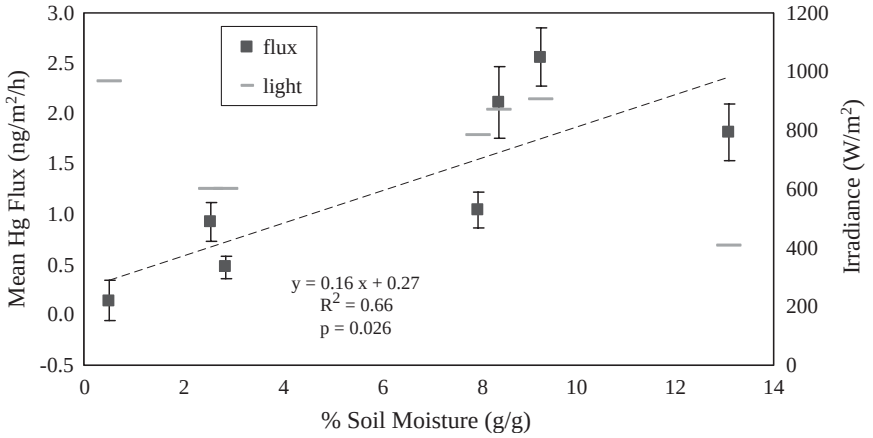

Fig. 5. Mean soil Hg flux at Desert 2 site measured between 11:00 and 13:00 as a function of percent moisture of soil. Error bars represent the standard error of the soil Hg flux. The corresponding mean solar irradiance for each flux measurement is plotted on the secondary y-axis.

and 11, respectively) and were only sampled during the daytime. Interestingly, in light conditions, flux data from the Agricultural, Grassland 6, and Pine Forest sites were not significantly different. For both the Agricultural and Pine Forest sites, light and then air Hg concentration were the most important variables in the MLR model. For the Grassland 6 site, relative humidity was most important. A cumulative ranking of variables from all sites indicated that light > air Hg concentration > relative humidity > temperature was the hierarchy of importance in predicting soil Hg flux. In dark conditions, air Hg concentration was the most important variable, followed by temperature, and then relative humidity.

Table 4 presents the SLR coefficients between soil Hg flux and the ancillary parameters measured in the study. In general there does not appear to be any consistency in pattern, with the exception that Hg flux in dark conditions shows a pattern of negative correlations, particularly with regard to temperature, for seven of the eight sites with dark data. Why would Hg fluxes increase as temperatures continually decreased during the night? Here we hypothesize the increasing fluxes are unrelated to the decreasing soil temperatures, and rather the increasing Hg fluxes are the result of the soil Hg pool replenishing in the absence of light. In addition, these correlations are strongest for the Grassland 1 site where fluxes were higher in the dark than in the light (see Table 2, Fig. 2).

We regularly observed diel Hg flux patterns in our data with maximum daytime fluxes of 1 to 2 ng/m^2/h; however, oftentimes no discernable diel pattern was observed, presumably, because the soil Hg flux was too variable, the instrumentation not sensitive enough, and/or other controlling parameters (i.e., changes in soil moisture or atmospheric oxidants) were not measured.

Based on data from the Desert 2 site, soil moisture appears to have a far stronger correlation to soil Hg flux than any of the other measured parameters. Fig. 5 shows a positive correlation between soil Hg flux and soil moisture based on average midday soil Hg fluxes. Recent research has shown that soils saturated beyond field capacity exhibit suppressed emission; however, when moisture is below saturation, fluxes from soils can be 2 to 5 times that occurring from dry soils (Gustin and Stamenkovic, in press).

Given the complexities in Hg cycling and noting the limitations of this study, which only sampled soil Hg flux over bare soils, we performed simple calculations to estimate natural emissions from soils in the contiguous U.S. using 2005 land cover statistics from the U.S. Geological Survey database (http://landcover.usgs.gov). Water, wetland, perennial ice snow, residential, commercial, industrial, and transportation areas were excluded, as they would constitute primarily anthropogenic sources of Hg emissions. The states Washington, Oregon, California, Nevada, and New Mexico were considered to be naturally enriched, and a mean flux of 4.2 ± 1.4 ng/m^2/h (based on previous Nevada scaling, Zehner and Gustin, 2002) was assigned to these areas. The remaining states, less quarry and mining areas, were considered background areas with a mean flux of 0.9 ± 0.7 ng/m^2/h using the value obtained from this study. Based on this crude scaling, the mean flux of Hg from soils in the continental U.S. would be 95 Mg/yr with a range of 44 to 150 Mg/yr based on one standard deviation. Mean flux from background soils was 43 Mg/yr (ranging from 9.6 to 77 Mg/yr), and mean flux from enriched soils was 52 Mg/yr (ranging from 34 to 69 Mg/yr). Other research has estimated wet deposition to be in the range of 5 to 16 μg/m^2/yr (Swain et al., 1992; Fitzgerald et al., 1994; Mason et al., 1994; Bullock et al., 1997; Grigal, 2002). This range is primarily representative of the eastern U.S. so using Mercury Deposition Network (http://nadp.sws.uiuc.edu/mdn) data for 2003, and extrapolating the few wet deposition data available for the rest of the western U.S., we estimated an average wet deposition to be ~60 Mg/yr. Assuming the magnitude of dry deposition is ~50% to 100% that of wet deposition (Bullock et al., 1997; Seigneur et al., 2004), the amount of Hg emitted from soils in the U.S. would roughly equal to the amount being deposited over terrestrial and aquatic ecosystems in a year's time.

5. Conclusion

Based on a large quantity of Hg flux data collected from bare soils with low Hg concentrations within the U.S., we determined an average Hg flux value of 0.9 ± 0.2 ng/m^2/h. Emission was the dominant flux although deposition was measured in dark conditions. Evasion of Hg from non-enriched soils was relatively low, and the majority of the fluxes ranged from 0 to 2 ng/m^2/h. We suggest that air Hg concentrations always be reported with soil Hg flux values and recommend manual injections of Hg in ambient air into Tekran analyzers be periodically performed before and after data collection as means of quality control when measuring soil Hg fluxes from background locations.

In this study, measurements were made over bare soil and much more work is needed in characterizing the role of vegetated surfaces as sources and sinks for atmospheric Hg before accurate Hg budgets can be constructed.

Here we monitored several parameters (air Hg concentration, soil temperature inside and outside of the chamber, air temperature, relative humidity, and solar irradiance) concurrently with soil Hg flux at these background sites and found that the parameters alone or combined could only weakly predict air–surface exchange of Hg at individual sites. Based on limited data from one site, there appears to be a significant correlation between percent soil moisture and soil Hg flux. By scaling up these and other field measurements, we estimate that ~100 Mg/yr of Hg is naturally emitted from soils in the contiguous U.S. and that this amount of Hg is similar to the amount being deposited to land, water, and vegetation surfaces on an annual basis.

Acknowledgements

Foremost, we thank Rick Zehner and Mark Engle for their help in collecting the soil Hg flux data presented in this report. Mark Engle also provided much guidance and generated the map of site locations. Research was funded by U.S. Environmental Protection Agency STAR, Electric Power Regulatory Institute (EPRI), and EEUC at the University of North Dakota. We also thank U.S.G.S. and James Rytuba for the use of a Tekran 2537A for this project. Thanks also to Rekha Pillai for Statsgo GIS work.

References

Bullock Jr OR, Benjey WG, Keating MH. Modeling of regional scale atmospheric mercury transport and deposition using RELMAP. In: Baker JE, editor. Atmospheric deposition of contaminants to the Great Lakes and coastal waters. Pensacola: SETAC Press; 1997. p. 322–47.

Carpi A, Lindberg SE. Application of a Teflon™ dynamic flux chamber for quantifying soil mercury flux: tests and results over background soil. Atmos Environ 1998;32(5):873–82.

Engle MA, Gustin MS, Zhang H. Quantifying natural source mercury emissions from the Ivanhoe Mining District, north-central Nevada, USA. Atmos Environ 2001;35:3987–97.

Engle MA, Gustin MS, Goff F, Janik CJ, Bergfeld D, Counce D, et al. Atmospheric mercury emissions from substrates amd fumraoles associated with three hydrothermal systems in the western United States. J Geolog Research submitted for publication.

Engle MA, Gustin MS, Lindberg SE, Gertler AW, Ariya PA. The influence of ozone on atmospheric emissions of gaseous elemental mercury and reactive gaseous mercury from substrates. Atmos Environ in press.

Ericksen JA, Gustin MS, Lindberg SE, Olund SD, Krabbenhoft DP. Assessing the potential for re-emission of mercury deposited in precipitation from arid soils using a stable isotope. Env Sci Tech submitted for publication.

Fitzgerald WF, Lamborg CH. Geochemistry of mercury in the environment. In: Lollar BS, editor. Treatise on Geochemistry. Amsterdam: Elsevier; 2003. p. 107–48.

Fitzgerald WF, Vandal GM, Mason RP, Dulac F. Air–water cycling of mercury in lakes. In: Watras CJ, Huckabee JW, editors. Mercury as a global pollutant: towards integration and synthesis. Boca Raton, FL: Lewis Press; 1994. p. 203–20.

Grigal DF. Inputs and outputs of mercury from terrestrial watersheds: a review. Environ Rev 2002;10:1–39.

Gustin MS. Are mercury emissions from geologic sources significant? A status report. Sci Total Environ 2003;304:153–67.

Gustin MS, Stamenkovic J. Mercury emissions from soils: effect of watering and soil water content. Biogeochemistry in press.

Gustin MS, Lindberg S, Marsik F, Casimir A, Ebinghaus R, Edwards G, et al. Nevada StoRMs project: measurement of mercury emissions from naturally enriched surfaces. J Geophys Res 1999;104(D17):21831–44.

Gustin MS, Lindberg SE, Austin K, Coolbaugh M, Vette A, Zhang H. Assessing the contribution of natural sources to regional atmospheric mercury budgets. Sci Total Environ 2000;259:61–71.

Kim K-H, Lindberg SE, Hanson PJ, Meyers TP. Micrometeorological measurements of mercury fluxes over background forest soils in eastern Tennessee. Atmos Environ 1995;29(2):267–82.

Lamborg CH, Fitzgerald WF, O'Donnell J, Torgersen T. A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients. Geochim Cosmochim Acta 2002;66(7):1105–18.

Lechler PJ. Modern mercury contamination from historic amalgamation milling of silver-gold ores in the Carson River, Nevada and Jordan Creek, Idaho: importance of speciation analysis in understanding the source, mobility, and fate of polluted materials. In: Ebinhaus R, Turner RR, de Lacerda LD, Vasiliev O, Salomons W, editors. Mercury contaminated sites: characterization, risk assessment and remediation. Berlin: Springer; 1999. p. 538.

Lindberg SE, Hanson PJ, Meyers TP, Kim KH. Air/surface-exchange of mercury vapor over forests—a need for reassessment of continental biogenic emissions. Atmos Environ 1998; 32(5):895–908.

Mason B, Moore CB. Concentrations in crust, granite, diabase (basalt), and shale. In: Principles of Geochemistry, 4th ed. New York: Wiley; 1982. pp. 46–47, 176–177.

Mason RP, Fitzgeral WF, Morel FMM. The biogeochemical cycling of elemental mercury: anthropogenic influences. Geochim Cosmochim Acta 1994;58:3191–8.

Mason RP, Abbot ML, Bodaly RA, Bullock Jr OR, Driscoll CT, Evers D, et al. Monitoring the response to changing mercury deposition. Environ Sci Technol 2005;39(1):14A–22A.

Nacht DM, Gustin MS. Mercury emissions from background and altered geologic units throughout Nevada. Water Air Soil Pollut 2004;151:179–93.

Poissant L, Casimir A. Water–air and soil–air exchange rate of total gaseous mercury measured at background sites. Atmos Environ 1998;32(5):883–93.

Poissant L, Pilote M, Casimir A. Mercury flux measurements in a naturally enriched area: correlation with environmental conditions. J Geophys Res Atmos 1999;104(D17):21845–57.

Rasmussen P, Edwards G, Kemp J, Fitzgerald-Hubble C, Schroeder W. Towards an improved natural sources inventory for mercury. Met Environ Int Symp Metallur Soc Can Inst Min Metall Pet (CIM) 1998:1–8.

Schroeder WH, Munthe J. Atmospheric mercury—an overview. Atmos Environ 1998;32(5):809–22.

Schroeder WH, Munthe J, Lindqvist O. Cycling of mercury between water, air, and soil compartments of the environment. Water Air Soil Pollut 1989;48(3–4):337–47.

Seigneur C, Vijayaraghavan K, Lohman K, Karamchandani P, Scott C. Global source attribution for mercury deposition in the United States. Environ Sci Technol 2004;38:555–69.

Swain EB, Engström DR, Brigham ME, Henning TA, Brezonik PL. Increasing rates of atmospheric mercury deposition in midcontinental North America. Science 1992;257:784–7.

Xiao ZF, Munthe J, Schroeder WH, Lindqvist O. Vertical fluxes of volatile mercury over forest soil and lake surfaces in Sweden. Tellus Ser B Chem Phys Meteorol 1991;43(3):267–79.

Zehner RE, Gustin MS. Estimation of mercury vapor flux from natural substrate in Nevada. Environ Sci Technol 2002;36:4039–45.

Zhang H, Lindberg SE. Processes influencing the emission of mercury from soils: a conceptual model. J Geophys Res 1999; 104(D17):21889–96.

Zhang H, Lindberg SE, Marsik FJ, Keeler GJ. Mercury air/surface exchange kinetics of background soils of the Tahquamenon River Watershed in the Michigan Upper Peninsula. Water Air Soil Pollut 2001;126:51–169.